

MASS SPECTROMETRIC MEASUREMENTS OF ATMOSPHERIC COMPOSITION

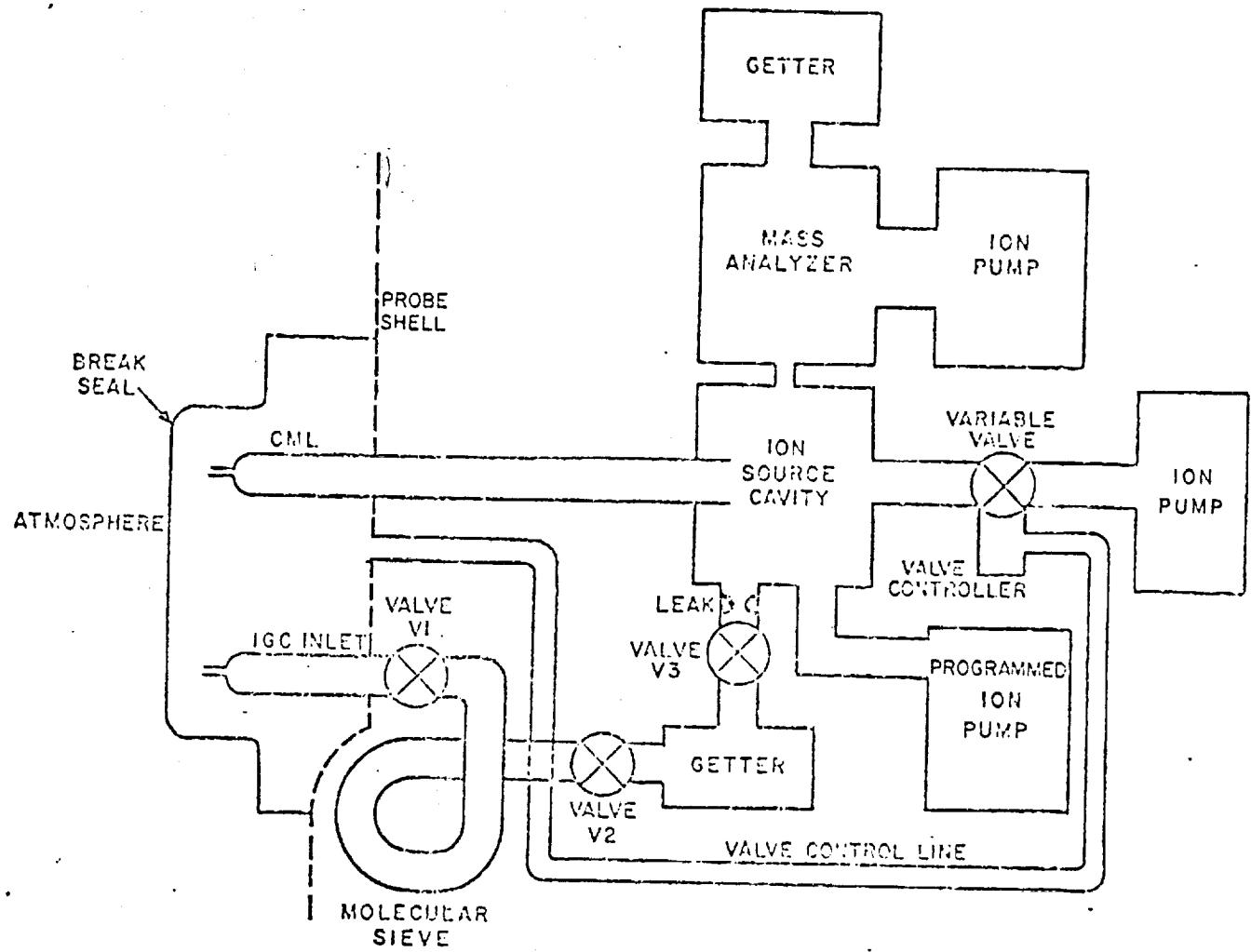
Dr. John H. Hoffman
University of Texas at Dallas

N75 20401

DR. HOFFMAN: The previous two speakers have given you two views of the usage of mass spectrometers in atmospheric studies. In addition, Dr. Spencer has spoken about various concepts of sampling the lower atmosphere from probes that descend into planets. I would like to continue in the vein that he has started and show you another system which we have been developing also for the Pioneer Venus program, and how it might be adapted to the outer planet probe studies which this conference is discussing.

Figure 8-14 shows a schematic drawing of such a system. The basic parts are the inlet, the pumping, and the mass spectrometer systems. We have proposed for Pioneer Venus and do so here, a continuous approach to sampling the atmosphere, whereas the previous speaker chose a batch approach, taking one sample, analyzing it and exhausting of pumping it out, and then at some time later taking in another sample. Our approach involves a continuous sampling and analysis of the atmosphere as the probe descends down to the surface. Its basic element is a leak, which is called a ceramic micro-leak, or CML, which protrudes outside the shell of the probe and into the streaming atmosphere as the probe descends to the surface. The gases are admitted through that leak which drops the pressure from the outside atmospheric pressure, which can be as high as ten or twenty bars, or even higher, to that required to operate the ion source in a single stage. In the case of Venus, these devices have been tested up to almost two hundred bars. The gas passing through the leak then travels through a very short, straight tube right into the ion source cavity, wherein ions are formed by electron bombardment. The ion beam is drawn out through a narrow slit into the mass analyzer. In our case, we propose a magnetic sector field analyzer, the same thing as Al Nier has shown you. The mass analyzer gives a quantitative determination of those gases in the ion source cavity.

Some of the characteristics of the leak are: it is made of a flattened stainless steel tube which has been oxidized on the



10 Bar Atmospheric Probe Mass Spectrometer

Figure 8-14

ORIGINAL PAGE IS
OF POOR QUALITY

inside; it can be pressed or forged together to get any given leak rate that you wish, between ten to the minus one to ten to the minus nine cc per second. This means, of course, that the leak rate can be tuned to whatever depth of the atmosphere you wish to fly. Of course, this cannot be done inflight. It must be adjusted in the laboratory ahead of time. In-flight the bases pass between the two parallel platelets of oxidized material, an oxidized metal, which is essentially a ceramic material and, therefore, the name ceramic micro leak. Owing to the inertness of the surface, there is a minimum change in the composition of the gas as it passes through the leak. The volume of the leak and its surface area are very small making the time response of the leak very small compared to the settling time of the probe in the atmosphere or the time of the sweeping of the mass spectrum, which will be discussed later.

Another part of the system consists of a pumping mechanism which in this case is an ion pump because of the expected large amount of helium in the entry planet atmospheres whereas on Venus the rare gases seem to be a very negligible part of the atmosphere. These gases do play an important role, but are negligible from the pumping standpoint. We have chosen here to use a constant speed pumping system and a variable valve, or variable orifice, which is controlled by the atmospheric pressure being fed in through a control line. It is sort of a pneumatic type valve. The conductance of the valve is directly proportional to the atmospheric pressure. This, then, maintains a constant pressure in the ion source, which has the great advantage of giving a wider dynamic range to the measurements. We actually obtain about ten to the seventh in dynamic range.

In addition to those parts, there is, of course, the mass analyzer, which I'll discuss more later. It is pumped separately by an ion pump which is used during entry and during pre-launch activities here on Earth, and a getter, which keeps the entire system, the vacuum part of this system, evacuated during pre-launch phase and the cruise phase to the planet, the seven years

PRECEDING PAGE BLANK NOT FILMED

or whatever it may take to get to some of the outer planets. The capacity of this getter is quite adequate, even against small leaks into the system, even if the probe were pressurized to one atmosphere, but I understand that the plans in general call for a nonpressurized probe. I think that eliminates the need for having vent tubes from the analyzer to the outside of the probe and the complications involved there in having to close these vents reliably so that you don't get the ten to twenty bar pressure leaking back into the instrument which would be a wipeout if that happened. We have a self-contained vacuum system here which takes no power, because these getters are room temperature operated getters. They are activated prior to launch in the laboratory, prior to the delivery of the instrument to the spacecraft.

Figure 8-15* is a photograph of an analyzer that was built for another purpose, but this is just to orient you to the size and shape of instruments that are being flown these days. This is a small sector field instrument. It consists of a magnet which bends the ion beam through different allowed trajectories through the magnet. This happens to be a three-channel instrument. By that we mean that, as ions are formed up in the ion source and pass down this inlet drift tube into the magnet, three different beams are identified coming out of the magnet. In this particular case, the mass ranges of one to four, to sixteen and sixteen to sixty-four atomic mass units are scanned simultaneously by a single sweep of the ion energy as the ions are formed in the ion source. By this means, of course, one can scan a wide mass range with a very small change in the voltage of the ion source itself, namely, in this case a factor of four rather than a factor of sixty-four. The instrument that we would propose for an outer planet mission would probably have two channels instead of three, and it would scan the mass range of one to four and twelve to forty-eight and perhaps on to mass sixty if we wish to cover iron. That extra mass range is essentially full. An even wider mass range is possible but these are some of many options that are available.

*Not available for inclusion in these proceedings

Figure 8-15

The instrument is packaged inside an eight inch diameter circle, and you can see it takes a very small total area of that circle. It can be packaged very readily, I would say, inside of the probe, as we saw yesterday.

The dynamic range, as I mentioned before, is approximately ten to the seventh. This is obtained as follows: we use an ion counting technique to detect the ions. We use electron multipliers which could be spiraltrons, magnetic strip type or venetian blind or Allen type multipliers. The counting rate that one can obtain effectively from these devices is something a little over 10^5 . That is the dynamic range of counts. In order to increase this to ten to the seventh, we use a little trick in the ion source. Where we find that we are coming up on a peak with a very high counting rate, one that is over some preset threshold, we automatically decrease the sensitivity of the ion source, cutting this by two orders of magnitude, and then count that specific peak at the lower sensitivity. This then expands the dynamic range and we can get seven decades. We can very nicely see one part per million species.

Figure 8-16 gives a few of the specifications of the mass spectrometer. I have talked about some of these already. We use a dual filament arrangement in the ion source just for redundancy. We have a multi-electron energy capability here whereby we can bombard the gases in the ion sources with different energy electrons. I will show you the effect of that a little later. The detectors have been discussed already. The ion source pressure is maintained in, say, the high ten to the minus six torr range, because this is a good range to get the sensitivity we mentioned and does not produce too much pressure scattering of the beam in the ion source. The analyzer is maintained at a very low range so that the peak shapes are very well confined. There are no significant tails, and one can effectively use the dynamic range that is available.

NEUTRAL MASS SPECTROMETER
DESIGN SPECIFICATIONS

- MAGNETIC-SECTOR MASS ANALYZER.
- MASS RANGE 1 TO 48 AMU.
- TWO CHANNELS: 1 TO 4; 12 TO 48 AMU.
- DYNAMIC RANGE 10^7 - EMPLOYS ION COUNTING TECHNIQUES.
- TWO ION SOURCE SENSITIVITIES - AUTOMATICALLY TRIGGERED BY ION BEAM COUNTING RATE.
- ION SOURCE: DUAL FILAMENTS
- MULTI ELECTRON ENERGY.
- DETECTORS: ELECTRON MULTIPLIERS.
- ION SOURCE PRESSURE: 7×10^{-6} TORR.
- ANALYZER PRESSURE: 10^{-8} TORR RANGE (ION AND GETTER PUMPED SEPARATELY FROM ION SOURCE).
- SPECTRAL SCAN TIME: 35 SECONDS AT 14 BPS.

Figure 8-16

The scan time of the mass spectrum is dependent, of course, upon the telemetry bit rates that are available. For this discussion, I have assumed the fourteen bits per second that are given in the little blue booklet of the ten bar probe summary. This gives a scan of about thirty-five seconds for the mass spectrum, which is repeated continuously as the probe descends through the atmosphere.

Now Figure 8-17 shows how one might utilize the different electron energies that are used to ionize the gas molecules in the ion source itself. These are three spectra here of carbon dioxide, and if you note very carefully here, there are about five decades of amplitude range compressed on these scales. What we are talking about here is a large peak amplitude difference that is compressed down to a very narrow range. Carbon dioxide has a parent peak at mass forty-four, has isotopic peaks of carbon and oxygen at forty-five and forty-six, and that might be a good way of determining what the isotopic ratios of carbon and oxygen are although I am not sure there would be enough CO_2 in the outer planet atmospheres to do that. This is more specifically related toward Venus. At one hundred volt electrons, or even seventy volt electrons, which is the range that is normally used in mass spectrometers flown on earth satellites, one has a multitude of peaks that are formed by dissociatively ionizing or by doubly ionizing complex molecules. You have a rather complex, a busy sort of spectrum here. At mass 44 we have the parent peak; at mass 28 we have the CO peak with perhaps the addition of a little nitrogen from air leakage into the system when this spectrum was taken. We have a doubly charged CO_2 peak at mass 22. The mass spectrometer measures the mass to charge ratio of an ion, so an ion with two charges will effectively appear in the spectrum at one half its mass, so that is CO_2 double plus. The sixteen is 0 and the twelve is C, from CO_2 , all torn out of the original molecules by the hundred volt electrons. Also, the fourteen peak seems to be significant here, which may indicate that there is some nitrogen in the mass twenty-eight peak.

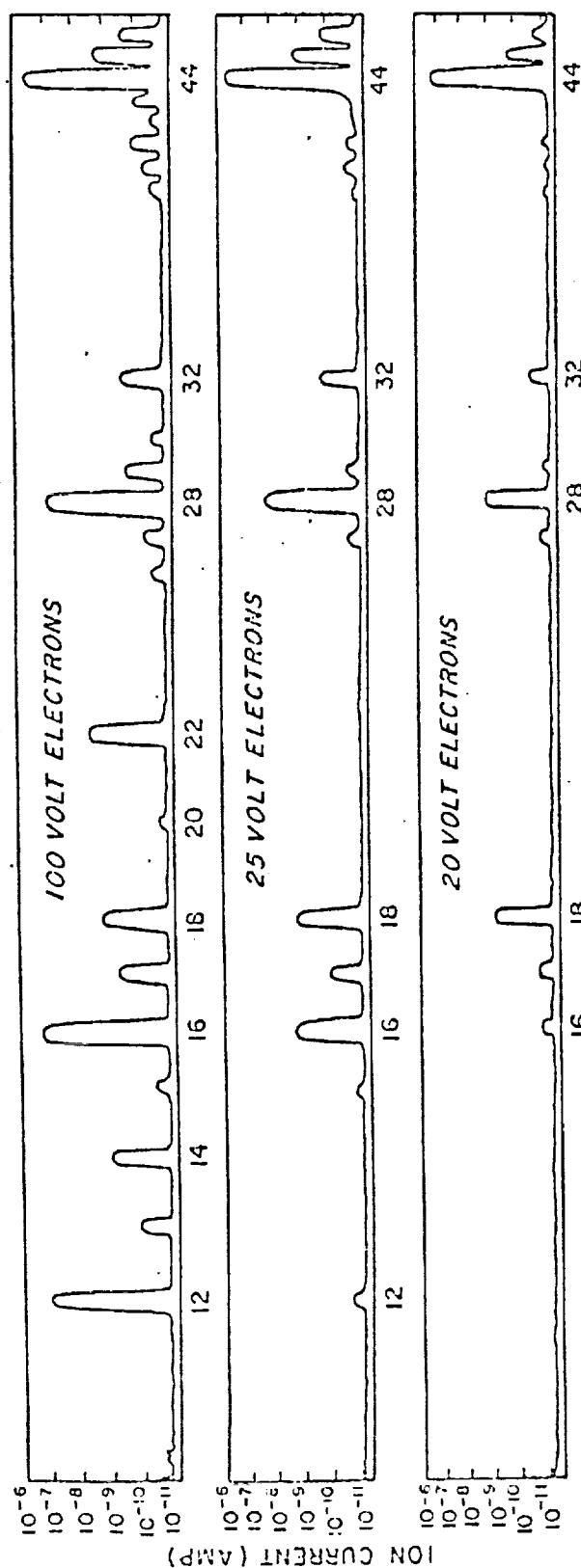


Figure 8-17

ORIGINAL PAGE IS
OF POOR QUALITY

Mass spectra of CO_2 produced by electron beams of 3 different energies.

Now, if we drop down to twenty-five volt electrons - these values are arbitrary, we can choose anything we wish - you see that the parent peak has not changed. In fact, it may have increased very slightly, indicating a slightly higher efficiency of ionization of the CO_2 at this level. The twenty-eight peak has decreased quite a bit. You will note that the twenty-two peak is absent completely, so one can eliminate from the spectrum there all doubly charged species. The eighteen has not changed - that's a water vapor impurity in the vacuum system itself. The sixteen has decreased significantly while the twelve has come down a real bunch. Therefore, the spectrum is much cleaner.

As we come on down now to the twenty-volt electrons, we find that, indeed, just about everything at the low end of the spectrum has been eliminated. The sixteen peak is almost gone. One thing to notice here is that the seventeen peak which is made in the ion source from the dissociation of water vapor - it is the OH ion and usually exists at something like one third the amplitude of the eighteen peak - has dropped almost two decades here; therefore, by using this technique, one could make a direct measurement of ammonia, which is at mass seventeen, without any significant interference of the OH from water vapor. One could make separate identifications of ammonia and water by this technique. Also, one might be able to measure the neon isotopes by the elimination of the doubly charged peak at mass twenty-two. The neon twenty-two, if there were enough CO_2 , is certainly going to be masked, but the CO_2^{++} can be eliminated from the spectrum by the lower energy. Incidentally, these doubly charged peaks tend to disappear at about 35 electron volts, which is well above the neon ionization potential.

This is actually a powerful tool that can be used for sorting out complex spectrums to identify the parent peaks and perhaps measure the isotopic ratios of a number of the different constituents, such as oxygen, nitrogen, and so forth, carbon.

Figure 8-18 gives an operations plan for entry into an outer planet atmosphere. From the time of entry, we have assumed

MASS SPECTROMETER OPERATIONS PLAN

TIME FROM ENTRY (minutes)

10 20 30 40

UNSTAGED ENTRY
NOMINAL ATMOSPHERE

○-NORMAL SPECTRUM
○,△-REDUCED IONIZATION
ENERGY SPECTRUM
△-IGC SPECTRUM

IGC

PRESSURE (bars)

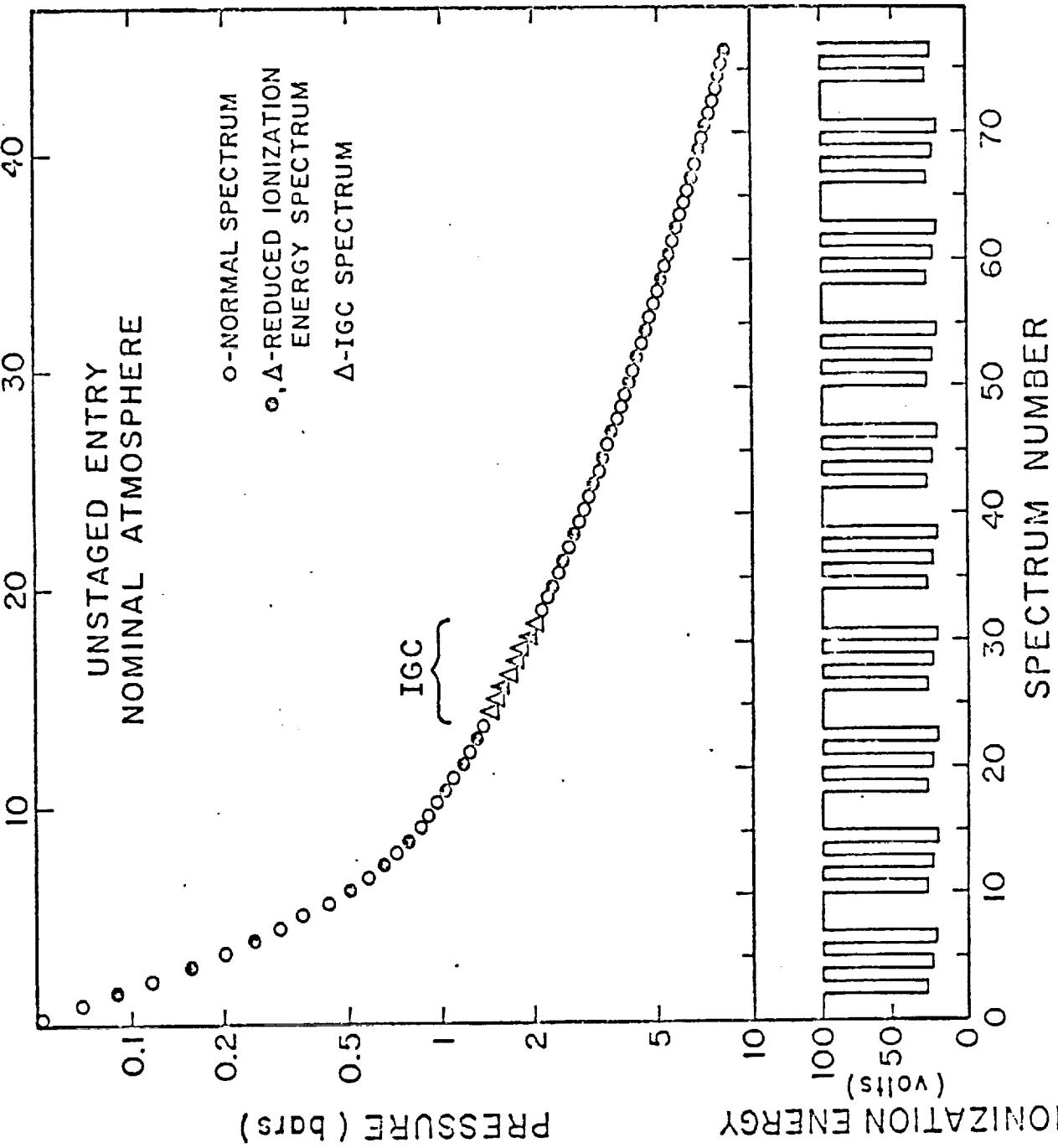


Figure 8-18

ORIGINAL PAGE IS
OF POOR QUALITY

a forty-five minute time to descend to about the ten bar level from fifty milibars. The circles indicate the time of each spectrum, which is thirty-five seconds. Again, this is assumed and is purely arbitrary and strongly dependent upon the telemetry bit rate that is available to us. The open circles are at one hundred volt electron energies; the solid circles at lower voltages. They are set up in blocks of eight. There are two sweeps of the spectrum at one hundred volts, then one at a lower voltage, which could be thirty, one again at one hundred volts then at twenty-two, one hundred, twenty, and one hundred. This grouping of eight, then, is repetitive as the probe descends. Now, this gives us a very good height profile of all the different constituents and enables one to make scale height determinations and study the variations as one goes through the cloud levels and that sort of thing.

There is one thing that I neglected to mention in the Figure 8-14. That is the IGC which stands for "inert gas cell." What we effectively do is to collect a sample of the atmosphere at the high level just after entry, just after the cap has been broken off, and the leaks have been exposed to the atmosphere. This sample is collected through another leak which has quite a bit larger conductance than the ion source leak. This sample is fed into a molecular sieve which purifies this gas sample of any active gas species, such as hydrogen in these planets. This sample is then transferred into a getter where it is further purified and sometime later in the flight, such as is shown by the triangles in the profile on the last slide, is transferred into the ion source. At that time, the programmed ion pump is operated which reduces the residual gas in the ion source. One can use this method to make isotopic ratio measurements of an enriched sample of the inert gases. One place where this might be very important is the situation that John Lewis mentioned yesterday, where one has normally an interference at mass three between HD, the molecule formed with the deuterium isotope of hydrogen, which comes in at mass three, and the helium three. In the mass spectrometer there is no way to distinguish between those two. Both of them appear

at mass three and they add, so we don't know the amount of each one. But if one had a purified sample of the atmosphere in which the hydrogen was essentially eliminated and then measured, one would have essentially no contribution from the H_D peak and could get a good measurement of the helium three, helium four ratio. This is then one of the little tricks that John referred to yesterday that can be used to determine the various isotopic ratio measurements of the inert gases and perhaps some of the active gases as well.

Figure 8-19 gives some mass spectrometer interface specifications. Again, these are somewhat subject to adaptations depending upon which type of a probe we are flying on, but basically we have a mass analyzer and base plate that weigh something like two kilograms. The magnet itself weighs less than one kilogram. The weight here is sort of dependent upon the strength of the base plate one might need to mount the instrument on to withstand the entry G's into those planetary atmospheres. The inlet assembly is fairly lightweight. It is a single CML and has one break-off seal which is kicked off just after entry. The inert gas cell is fairly light. The pumps are approximately a kilogram. The electronics depend a little on what mass ranges we would cover and its degree of sophistication. Three kilograms is a good value giving a total weight of close to seven kilograms. The volume is around seven and one half liters, and this is again somewhat adjustable. The shape is certainly adjustable, as one can package electronics different ways and make this thing adaptable to the different probe designs. The power is around eleven watts. This is a rather steady power, because there are no pyrotechnic devices in the instrument after the initial ejection of the cap. There is some power reserve in here for heating of the inlet devices to prevent condensation on the inlet tube or on the leak itself.

The telemetry format depends upon what is available to us. We are assuming a fourteen bit per second read out rate. Each spectral scan, in the particular design that I showed you requires about four hundred ninety bits, that is out to mass forty-eight.

NEUTRAL MASS SPECTROMETER
INTERFACE SPECIFICATIONS

• WEIGHT (KG)	
ANALYZER AND BASEPLATE	2.0
INLET ASSEMBLY	.4
INERT GAS CELL	0.3
PUMPS	1.2
ELECTRONICS	3.0
	<hr/>
	6.9 KG

- VOLUME 7500 CM³
- POWER 11.5 WATTS
- TELEMETRY

490 BITS PER SPECTRAL SCAN (49-10 BIT WORDS)
TELEMETRY WORDS SHOULD BE EQUALLY SPACED IN TIME.
SPECTRAL SCAN TIME = 35 SEC.
READOUT RATE: 14 BPS

Figure 8-19

ORIGINAL PAGE IS
OF POOR QUALITY

We use ten bit words, of which one bit is the sensitivity flag, and nine bits contain a sort of a pseudo-logarithmic format to the base two. This format gives a 6-bit accuracy over the entire dynamic range. This information is telemetered back to earth along with about eighty bits of overhead during each of the sweeps of the mass spectrum; overhead being status flags, housekeeping data, and that sort of thing, engineering type units.

What I have tried to show you is one system which we could use to sample and measure the atmosphere of the outer planets. It is adapted from our Pioneer Venus instrument. All the parts of this system have been tested in the laboratory and have been shown to be within the "state-of-the-art" of space mass spectrometry.

L. POLASKI: I think we have time for a quickie question. Joel kind of played it smart. He didn't allow the other fellows to get questions. If you have a question for any one of the first three, throw it out.

QUESTION: How long does it take you to completely evacuate the chamber for a new sample gas and how completely do you get rid of all the previous molecules when you get a new sample in there to analyze?

DR. HOFFMAN: We have done some tests along that line and we show that in about a two-second time frame, we can pump out a gas like argon with an ion pump to about four percent of its original level. Argon is notoriously slowly pumped by ion pumps; all the rare gases are. The active gases will pump out much faster than that. Two seconds to get down to about the four percent level for argon is an actual test number that we have done in the laboratory. I would say in a few seconds between each scan of the spectrum, we would have the system pretty well evacuated so that we would have very little cross contamination of the different sweeps. In other words, we would really be looking at a fresh spectrum of gas, a fresh sample of gas, each time.

QUESTION: Are there any entry velocities on the breakdown system in the operation of the instrument itself?

MR. SEIFF: Are you talking about high velocity penetration at high velocity entry?

MR. HOFFMAN: This type of a system is not the type that Al Nier was talking about where one uses the ram energy due to the motion of the vehicle itself through the medium to bring the gas samples in. Here, the gas is sampled as it slips past the probe as it is settling through the atmosphere after entry. The curve I showed you is for non-staged type entry. This is just the settling rate of the probe itself through the atmosphere. It is a terminal velocity. It is not particularly critical in that case.

QUESTION: Do you propose using getter material for keeping out gases on this cruise? For the outer planets, we are talking about a rather long cruise. Is it still possible to use getter material?

MR. HOFFMAN: I did a calculation knowing the actual tested capacity of the getters that we are proposing here. If we had an atmospheric probe that had one atmosphere of a gas in it, say nitrogen, or it doesn't matter which gas particularly, as long as it is not a rare gas, we could pump for, like, ten years against a leak of ten to the minus ten cc per second, and that is readily achievable with today's techniques of building vacuum systems. We can also absorb in this getter a number of monolayers of gas off the internal surface of the instrument. I think we have more than adequate capacity without having to resort to vent tubes that stick outside the probe.